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Smooth $YBa_2Cu_3O_{7-x}$ thin films prepared by pulsed laser deposition in O_2/Ar atmosphere

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We report on pulsed laser deposition of $YBa_2Cu_3O_{7-x}$ in a diluted O_2/Ar gas resulting in thin epitaxial films which are almost outgrowth-free. Films were deposited on $SrTiO_3$ or MgO substrates around 800 °C at a total chamber pressure of 1.0 mbar, varying the argon partial pressure from 0 to 0.6 mbar. The density of boulders and outgrowths usual for laser deposited films varies strongly with Ar pressure: the outgrowth density is reduced from 1.4×10^7 to 4.5×10^5 cm^{-2} with increasing Ar partial pressure, maintaining a critical temperature $T_{c,zero}\approx90$ K and a transport critical current density $J_c(77\text{ K})\geq10^6$ A/cm^2 by extended oxygenation time during cool down.

Pulsed laser deposition (PLD) is now a well established method for preparation of thin films. Indeed, it seems to be the most widespread method for deposition of thin films of ceramic superconductors such as $YBa_2Cu_3O_{7-x}$ (YBCO or 1-2-3). Many groups routinely produce YBCO thin films of high quality by PLD and numerous studies of optimization of the PLD process have been published.[1,2] A general feature of YBCO thin films, irrespective of the deposition technique[3–5] used, is surface *outgrowths*. Outgrowths are misoriented and/or off-stoichiometric crystallites appearing as large particles (0.1–0.5 μm diameter) on the film surface. Typical reported[4,6] densities are 10^8–10^{10} cm^{-2}. A particular feature of PLD films are *boulders* or *droplets*.[7] These are spherical particles (0.1–1 μm diameter) appearing on the film surface. Both kinds of surface particles are hazardous to multilayer structures, since typical film thicknesses are below 300 nm. It is in fact possible to grow films with a very small number of particles in a narrow region of deposition parameters.[5] The authors' experience is that this region is so narrow that small fluctuations in, e.g., laser output will influence the surface quality, though leaving the electrical properties of the films unchanged. New geometries for PLD have been proposed[7–9] in order to solve the particle problem. We present here our results from deposition in an O_2/Ar atmosphere resulting in a substantial reduction of outgrowths. We have used the standard geometry, where the substrate surface is facing the target.

Our deposition chamber was pumped to a base pressure of 10^{-6} mbar by a diffusion pump stack equipped with a liquid-nitrogen cold trap. Before deposition, the diffusion pump was turned off and allowed to cool down thereby only pumping through the rotary pump. Pressure was monitored with a capacitance manometer and kept constant by an automatic regulator. The P(O_2):P(Ar) ratio was set by adjusting the individual gas flows regulated by two calibrated mass flow controllers (relative uncertainty ~3%). A stainless-steel pellet served as substrate heater block and was heated on the back side by the radiation from a halogen lamp. The temperature was monitored with a Pt/Pt-Rh thermocouple soldered into a hole in the pellet. The substrate was glued on to the pellet with silver paint for good thermal contact. A commercially available stoichiometric $YBa_2Cu_3O_{7-x}$ target (Jupiter Technologies Inc.) was clamped to a water cooled stage 42 mm below the substrate surface. The light pulses (248 nm, 30 ns) from a KrF excimer laser (Questek 2720) were focused on the target with a spot size of 1.6×2.9 mm^2. The fluence was 1.3 J/cm^2 and the repetition frequency 10 Hz. A motorized mirror allowed the laser beam to be scanned over an area of 10×10 mm^2 on the target. Each film deposition corresponded to one scan (120 s) yielding a film thickness of 170 nm and a mean deposition rate of ~1.4 nm/s. The thickness was measured with a profilometer on each film after it was patterned for critical current density (J_c) measurements by photo lithography and H_3PO_4 wet etch. Prior to deposition the chamber was filled to 1.0 mbar with the appropriate gas mixture and the substrate was allowed to thermalize at 800 °C for 10 min. The total gas flow was 9.5 sccm. Deposition was performed on (001) oriented $SrTiO_3$ substrates at 805 °C and on (001) oriented MgO substrates at 785 °C. All substrates were $8\times8\times0.5$ mm^3. After deposition the chamber was flooded with oxygen to atmospheric pressure and the substrate was slowly cooled down to room temperature. The sample data presented here are representative for YBCO on $SrTiO_3$, but the results and trends have been reproduced on MgO equally well, although films on MgO substrates tend to yield T_c's about 0.5 K below those on $SrTiO_3$.

Films deposited in pure oxygen (e.g., sample A) were cooled at a rate of 8.5 °C/min to 550 °C and at 2.8 °C/min to 300 °C. This was followed by cooling to room temperature as quickly as possible (typically 25 min). The films have a superconducting transition temperature $T_{c,zero}=90.5$ K. The transport critical current density at 77 K for the listed sample A was measured on a 100-μm-wide strip to be $J_c(77\text{ K})\approx1.4$ MA/cm^2. The scanning electron micrograph in Fig. 1(a) shows the film surface to be covered by outgrowths at a density of $\sim1.4\times10^7$ cm^{-2}. Boulders were observed at a density of $\sim3\times10^5$ cm^{-2}. Besides the substrate peaks, powder x-ray diffraction [Fig. 2(a)] reveals only the YBCO (00ℓ) reflections, indicating that the films are highly c-axis oriented with no randomly oriented 1-2-3 phase. Only a small peak at $2\theta=41.7°$ (d value 2.16 Å) indicate a trace of foreign phases. This *could* be the 311 reflection from Y_2BaCuO_5 (green phase) or the 422 reflection from Y_2O_3.

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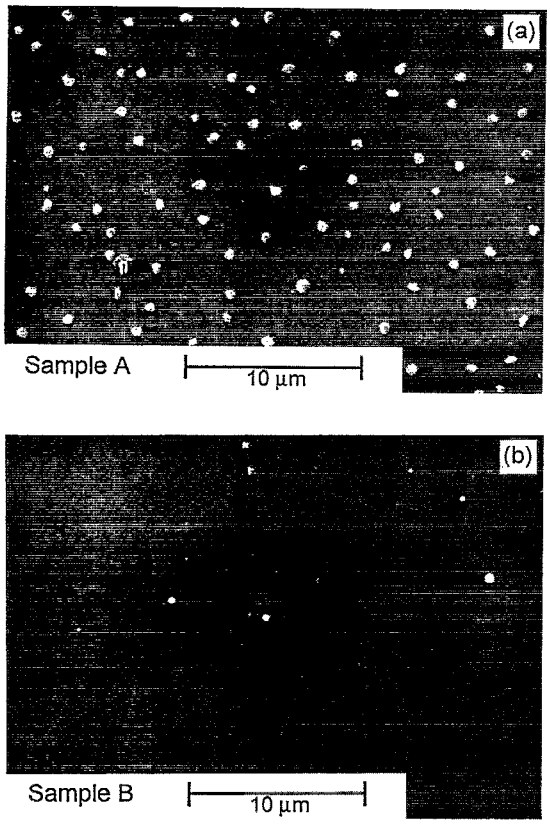

FIG. 1. Scanning electron micrographs of the film surfaces. (a) Sample A [$P(O_2)$:P(Ar)=1.0:0 mbar], outgrowth density $\sim 1.4\times10^7$ cm^{-2}. (b) Sample B [$P(O_2)$:P(Ar)=0.4:0.6 mbar], outgrowth density $\sim 4.5\times10^5$ cm^{-2}. This micrograph was focused on a typical round boulder.

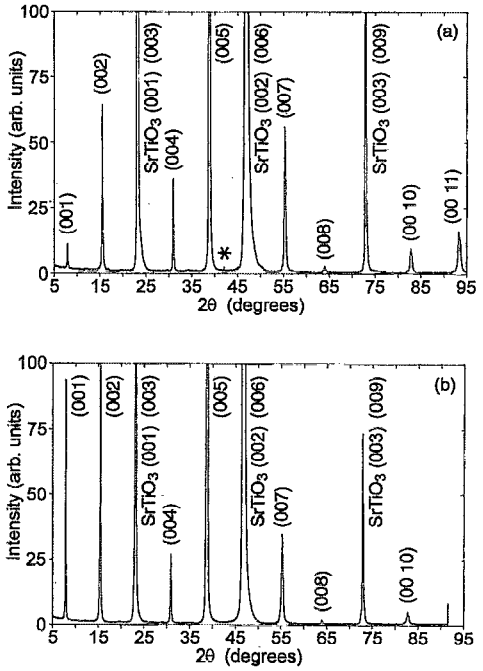

FIG. 2. Powder x-ray diffraction of the films. (a) Sample A [$P(O_2)$:P(Ar)=1.0:0 mbar], besides the substrate peaks and a small peak at $2\theta=41.7°$ (at *), only the YBCO (00ℓ) reflections are revealed. (b) Sample B [$P(O_2)$:P(Ar)=0.4:0.6 mbar], only substrate and YBCO (00ℓ) reflections are seen.

Both reflections are low intensity reflections, so this is not very likely. No definite conclusion about the 41.7° peak can be reached at this point.

As argon is substituted for oxygen, a notable change in the visible part[10] of the ablation plume is seen. The plume becomes more diffuse and bluish as the argon partial pressure is increased. In pure oxygen the plume appears very directional and flame-like with a red/purple color. Films deposited in argon diluted oxygen (O_2 partial pressures in the range 0.5–1.0 mbar) exhibit less outgrowths and almost unchanged electrical properties, using the same cool-down procedure as for deposition in pure oxygen. At O_2 partial pressures below 0.5 mbar T_c decreases substantially. At 0.4 mbar O_2 T_c dropped to 83.5 K. After several experiments with the cool-down procedure we found that a decrease in the cooling rate to 1.4 °C/min in the temperature span 550–300 °C increased the critical temperature to $T_c=90$ K (e.g., sample B). A similar cooling procedure applied to a sample deposited in pure oxygen has been observed *not* to cause changes in the outgrowth density. The transport critical current density was measured on a 20-μm-wide strip to be $J_c(77\ \text{K})\approx 3.8$ MA/cm^2. Figure 1(b) shows the surface of sample B to be almost outgrowth-free with a density of $\sim 4.5\times10^5$ cm^{-2}. The density of boulders is $\sim 1.1\times10^6$ cm^{-2}. Powder x-ray diffraction [Fig. 2(b)] reveals only the (00ℓ) reflections from the 1-2-3 phase and the substrate. There are no traces of foreign phases. This indicates that the reflection at $2\theta=41.7°$ for sample A is correlated with the high density of outgrowths on this sample.

We note that within the accuracy of our x-ray diffraction data we observed an elongation of the c-axis for samples which did not experience prolonged cooling (those with the low T_c's). The longer c-axis corresponds to oxygen deficiency,[11] hence reduced critical temperature. This observation agrees well with the longer oxygenation time needed for obtaining T_c's around 90 K.

The surface particles were identified and counted from scanning electron micrographs similar to those in Fig. 1. A certain magnification is necessary in order to positively identify boulders and outgrowths. Even when averaging over some micrographs the relative uncertainty on the numbers becomes large when only 0–5 particles are identified on each micrograph. This corresponds to densities below 10^6 cm^{-2} having an uncertainty of a factor of ~2. The observed change in boulder density for the two samples is therefore not noteworthy. For densities around 10^7 cm^{-2}, the relative spread is much smaller yielding an uncertainty of ~20%. Sample to sample variations seem to lie within these uncertainties.

The increase in the oxygenation time necessary for the smooth sample (sample B) may be explained in at least two ways. One possible explanation is that oxygenation during deposition is reduced critically due to the lower oxygen partial pressure (here it must be noted that in *pulsed* laser deposition each blast of material will last from[12–14] 10–100 μs yielding correspondingly high peak deposition rates from 14–1.4 μm/s, 0.14 nm/pulse). Another explanation involves

oxygen diffusion in YBCO at temperatures below the tetragonal-orthorhombic transition temperature. It is assumed[15] that transport of oxygen in and out of YBCO thin films mainly takes place through structural imperfections breaking the film surface (serving as O_2 channels) and not through the perfect solid/ambient interface. The oxygen in-diffusion thus is critically dependent on the density of imperfections. Imperfections could be grain boundaries, precipitates, and outgrowths. Since sample B has a factor of 30 fewer outgrowths as compared to sample A, this oxygen diffusion mechanism may well explain the necessity for a longer oxygenation period.

Outgrowths and precipitates in $YBa_2Cu_3O_{7-x}$ thin films have been studied intensively.[3,4,6] Precipitates incorporated in the films are for the most Y_2O_3 at densities[3,6,16] from 10^{15} to 10^{18} cm^{-3}. Outgrowths in sputtered films have been identified[3,4] as Y_2O_3, CuO, or $CuYO_2$ grains and composites of YBCO, CuO, and Y_2O_3. Cu-rich outgrowths have been observed[6] to nucleate on large Y_2O_3 inclusions which are not incorporated orderly in the YBCO lattice. It is known that large clusters of Y_2O_3 and other metal oxides are present in the plasma generated during PLD.[10,17–20] An obvious assumption would be that these clusters are incorporated in the film as precipitates serving as nucleation sites for outgrowths. Substituting Ar for O_2 in the process gas might lead to lower chemical reaction rate and enhanced elastic scattering in the plume, thereby reducing the condensation and deposition rates of clusters.

In summary, we have produced epitaxial YBCO thin films with $T_c \approx 90$ K and $J_c(77\ \text{K}) \approx 3.8$ MA/cm^2 and with a surface outgrowth density as low as 4.5×10^5 cm^{-2} by pulsed laser deposition in an O_2/Ar atmosphere. At low O_2 partial pressures, a longer oxygenation time during cool down was needed in order to obtain the high T_c's.

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